

Reactive Applications of Cyclic Alkylene Carbonates

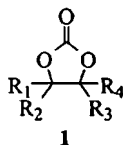
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The synthesis and use of cyclic alkylene carbonates as reactive intermediates first appeared in the literature more than 50 years ago. However, the range of their usefulness in industrial applications has only been fully realized in the past decade. In this article, numerous reactive applications of the cyclic alkylene carbonates, specifically the five-membered cyclics, are discussed. In addition, utilization of the chemistry presented in this review for the preparation of industrially useful monomers, polymers, surfactants, plasticizers, cross-linking agents, curing agents, and solvents, to name a few, is also discussed.

Introduction

Five-membered alkylene carbonates (1,3-dioxolan-2-ones) of the general structure



have been the subject of considerable research. In particular, ethylene carbonate (EC, $R_{1-4} = H$) and propylene carbonate (PC, $R_{1-3} = H$, $R_4 = CH_3$) have been available commercially for over 40 years.¹ For this reason, much of the following review focuses on research involving these two materials. Since their commercialization in the mid-1950s, EC and PC have found numerous applications as both reactive intermediates and inert solvents. A quick examination of their physical properties (Table 1)² is all that is needed to appreciate why EC and PC are attractive solvent substitutes. In addition to their biodegradability³ and high solvency,⁴ they have high boiling and flash points, low odor levels and evaporation rates,⁵ and low toxicities.⁶ The use of PC as a solvent in degreasing,⁷ paint stripping,⁸ and cleaning⁹ applications has risen dramatically in the past few years. In addition, EC and PC are finding increased utility as diluents for the epoxy¹⁰ and isocyanate¹¹ components of 2K resin systems, and they have become the electrolytes of choice in the production of lithium ion batteries.¹² PC also finds utility as a carrier solvent for topically applied medications and cosmetics.¹³ Although much can be said concerning the use of these alkylene carbonates as inert media, their potential as reactive intermediates is the primary focus of this discussion.

Although a number of methods exist to synthesize five-membered alkylene carbonates of structure 1, carbon dioxide insertion into the appropriate oxirane is the commercial method employed to synthesize the most common of these, EC, PC, and butylene carbonate (BC, $R_{1-3} = H$, $R_4 = C_2H_5$). Typically, an alkylammonium halide catalyst such as tetraethylammonium bromide^{1a,b} is employed (Figure 1). The alkylene carbon-

Table 1. Properties of Ethylene and Propylene Carbonate

property	EC	PC
boiling point (°C)	248	242
freezing/melting point (°C)	36.4	-49
flash point (°C)	160	135
viscosity (cP, 25°C)	2.56 ^a	2.50
% VOC ^b (110 °C)	34	28

^a Supercooled liquid. ^b Volatile organic content.

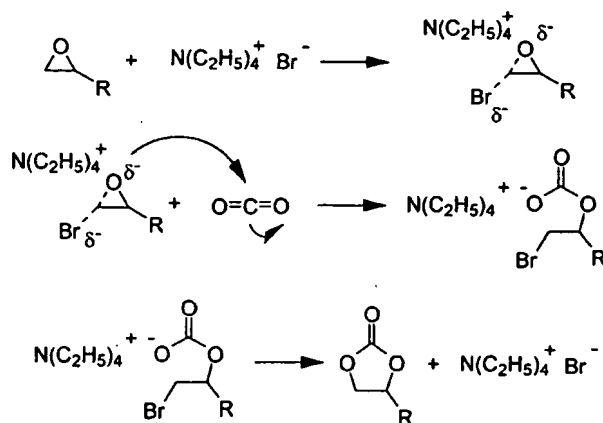


Figure 1. Synthesis of five-membered alkylene carbonates via insertion of CO₂ into oxiranes. R = H, CH₃, or C₂H₅.

ates produced react with aliphatic and aromatic amines, alcohols, thiols, and carboxylic acids. Under certain conditions, they can also undergo ring-opening polymerization. It is the intent of the author to discuss each type of reaction in detail, from the reaction mechanism and conditions required to a brief description of the applications in which each reaction finds utility. In addition, the synthesis and utility of unique alkylene carbonate derivatives is also discussed. In this way, a general overview of alkylene carbonates as reactive intermediates is intended. Shaikh and co-workers¹⁴ recently published a review of organic carbonates in which several applications of alkylene carbonates are discussed in addition to those of linear carbonates. However, the use of these materials has risen dramatically in the past few years and has grown to encompass several additional areas of active research.

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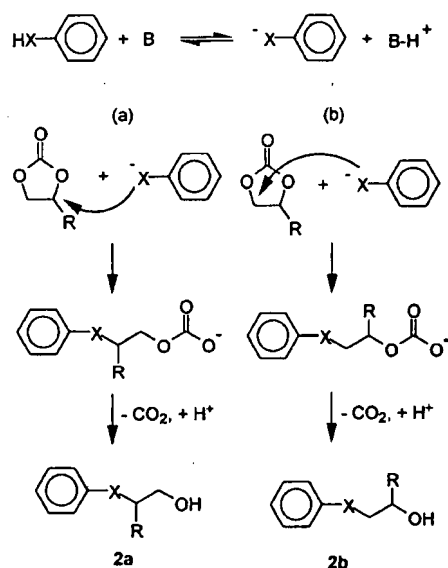


Figure 2. Reactions with aromatic active-hydrogen-containing moieties produces a mixture of isomers 2a and 2b. X = O, NH, or S. B indicates to any alkali.

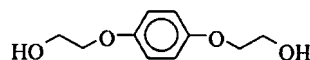
Reactions with Aromatic Amines, Alcohols, and Thiols

Alkylene carbonates, particularly 1,3-dioxolan-2-ones, can be used to alkylate active-hydrogen-containing aromatics such as phenol and phenolic resins,¹⁵ thiophenols,¹⁶ aniline,¹⁷ and the like in the presence of alkali catalysts. The general reaction scheme is illustrated in Figure 2. Note that X can be O, NH, or S. Nucleophilic attack at either alkylene carbon is followed by loss of carbon dioxide to obtain 2a and 2b in a 50/50 \pm 10 ratio of isomers for R = CH₃. The list of catalysts useful in this reaction is quite long and includes phosphines¹⁶ and phosphonium halides,^{16b} alkali metals,^{15b} tertiary amines,¹⁸ alkali metal halides,^{15a} hydroxides,^{15b} carbonates,^{16a} and alkoxides.^{15b} Typically, temperatures in the range 100–150 °C are required for alkylation of amines and thiols, whereas higher temperatures in the range of 150–200 °C are required for alkylation of alcohols. In such reactions, the alkylene carbonate order of reactivity is R=H > R=CH₃ > R=C₂H₅.

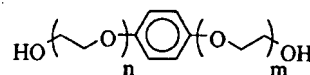
It is well-known that the products shown in Figure 2 can be obtained more directly by reaction with oxiranes such as ethylene oxide (EO) and propylene oxide (PO). The oxiranes are less expensive than their corresponding alkylene carbonates, especially considering that 44 g/mol of carbonate is lost in the form of CO₂ and that alkylation proceeds at lower temperatures. However, alkylene carbonates offer significant advantages over oxiranes in this application. The alkylene carbonates are far less hazardous materials, requiring fewer safety protocols.⁸ In addition, alkylation employing an alkylene carbonate does not require the high-pressure equipment often necessary when working with the highly volatile oxiranes. Most notably, however, is that alkylation employing alkylene carbonates does not require the use of solvent. In most cases, the carbonate acts both as reactant and as solvent. This last advantage is key in the alkylation of aromatic substances that have high melting points or are otherwise difficult to handle.

An illustrative example of alkylation is the reaction of hydroquinone (1 mol) with EC (2 mol) to synthesize

1,4-bis(2-hydroxyethoxy)benzene, commonly known as HQEE¹⁶

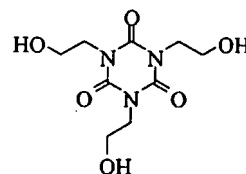


HQEE is a useful spacer in the synthesis of chemically and thermally stable, high-strength polyurethanes that find application in skateboard wheels and tractor tires.¹⁹ Hydroquinone (mp = 172–175 °C) forms a homogeneous liquid with EC when heated to approximately 100 °C. Continued heating to 160 °C gives alkylation and CO₂ evolution, which can be monitored either visually or using a CO₂ analyzer to determine reaction rate and time required. The product, an off-white solid with a melting point of 100–102 °C, can be flaked or handled in the molten state without the added cost of solvent removal. In addition, the alkylene carbonate method is much more selective with respect to the molecular weight distribution of the product obtained. Whereas several moles of EO or PO will react at each site, producing the following material²⁰



in which $n + m = 0-4$, EC and PC react at each site only once. The result is a product that does not contain ether linkages, a benefit when chemical and thermal stability is desired in the final application. Other examples of alkylation via reaction with alkylene carbonates include the reaction of EC and PC with cardanol (a product derived from cashew nut oil) to produce useful plasticizers²¹ and with resorcinol to produce a lower-melting alternative to the polyurethane spacer HQEE.²² The latter reference features the reaction of resorcinol with EC/PC blends to create a mixture of alkylation products.

An illustrative example of *N*-alkylation is the reaction of cyanuric acid (1 mol) with EC (3 mol) to form 1,3,5-tris(2-hydroxyethyl)isocyanurate (THEIC)¹⁸



As with hydroquinone, cyanuric acid (mp > 360 °C) forms a homogeneous solution with EC at temperatures well below that required for alkylation to proceed. The product, an off-white solid with a melting point of 136–140 °C, can be prepared without the need for solvent. THEIC is a cross-linking agent employed in the preparation of polyester resins. Resins prepared from this material exhibit the corrosion resistance necessary to coat electrical cables that are laid along the ocean floor. The presence of ether linkages typical of the EO alkylation product would adversely affect the performance of the final product.

Reactions with Carboxylic Acids

Five-membered alkylene carbonates react with carboxylic acids in much the same way as with aromatic active-hydrogen-containing moieties.²³ Similar catalysts

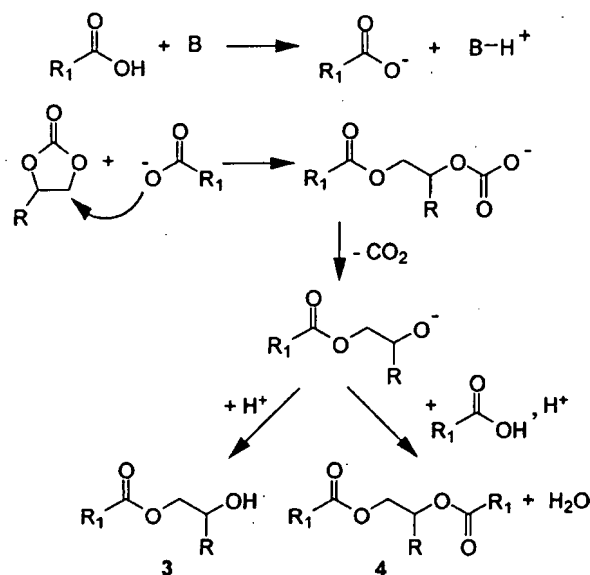


Figure 3. Reactions with carboxylic acids produce a mixture of hydroxyalkyl esters **3** and diesters **4**. Note that only one of two possible isomers of **3** is shown.

and reaction temperatures are required. The reaction is classified as an alkylation/esterification that involves nucleophilic attack at either alkylene carbon (Figure 3). However, a mixture of products **3** and **4** is produced in addition to two isomers of **3** should $R \neq H$. An example is the reaction of benzoic acid with EC. Apicella and co-workers employed a 260% excess of EC to obtain **3** as the predominant product.^{23b} However, Yoshino et al. found that a mere 10% excess could be effective using a triethylammonium iodide catalyst in combination with a shorter reaction time. In this manner, reacting EC with benzoic acid at 140–145 °C for 0.7 h resulted in an 86.5% yield of **3**.^{23a} Although this selectivity represents a drawback to the pure synthetic chemist, it has been exploited to synthesize prepolymers.²⁴ Researchers at Reichhold reacted EC and PC with multifunctional carboxylic acids such as terephthalic acid to synthesize polyester oligomers. These hydroxy-functional oligomers were then reacted with simple diols and unsaturated anhydrides to give unsaturated polyesters useful in composites for the aerospace industry.

In addition to prepolymer synthesis, the above chemistry also finds use in polymer modification. EC has been reacted with poly(ethylene terephthalate) (PET) polyesters in an effort to reduce the acid number of the material. PET polyesters are excellent materials for industrial conveyor belts that operate under heavy loads and at high speeds. However, degradation of the polymer can occur over time, resulting in reduced tensile strength and even visible cracking. Researchers at Allied discovered that a more chemically resistant material could be obtained simply by reacting the polymer with EC, thereby reducing the number of carboxylic acid end groups at which degradation typically occurs.²⁵ The modification procedure follows the polycondensation of dimethyl terephthalate or terephthalic acid with ethylene glycol and involves the addition of an alkali metal salt such as potassium iodide. Typically, 0.5–1.0 wt % EC is added and allowed to react at 280 °C for 5–15 min. The result is a material with an acid number of <3 (mg of KOH/g) as compared to approximately 20 for the untreated polymer. Cape

Table 2. Modification of SAPs with Alkylene Carbonates to Improve AAP Performance

carbonate employed	time at 215 °C	FSC (g/g)	AAP (g/g)
—	—	39	11
EC	15	37	30
PC	20	37	31
PC	30	36	33
BC	20	37	30

Industries has employed PC in a similar application. In this case, the low-acid-number PET material reacts much more quickly with isocyanates to produce polyurethane foams.²⁶ The foams produced exhibit the improved surface adhesion necessary for the production of laminate foam board.

Yet another useful example of polymer modification by reaction with five-membered alkylene carbonates takes advantage of the diester product **4** as a cross-link site. Lightly cross-linked sodium polyacrylate is a hydrophilic material that absorbs many times its weight in water yet does not dissolve. This property makes the material useful as a superabsorbing media for sanitary articles such as diapers and feminine hygiene products.²⁷ However, the liquid-filled material is easily deformed by an external pressure such as the sitting action of a child, resulting in unwanted discharge of the absorbed liquid. Traditionally, researchers have modified superabsorbent polymers (SAPs) of this type by further reacting them with simple, nontoxic diols or triols such as propylene glycol or glycerine.²⁸ However, researchers at Stockhausen have found that alkylene carbonates can also be used in this application.²⁹

Table 2 shows the performance of a typical superabsorbing polymer (SAP) before and after modification with EC, PC, and BC.²⁹ In each case, alkylene carbonate, water, and ethanol (2.0 g each) were mixed with 100 g of the polymer to be modified. The mixture was then placed in an oven preheated to 215 °C and allowed to react for 15–30 min. The performance of the resulting powder was quantified by the following tests: (1) free swell capacity (FSC), the amount of saline solution (0.9% NaCl) retained by the polymer upon immersion in said liquid for 30 min; (2) absorbency against pressure (AAP), the amount of saline solution retained by the polymer upon immersion in said liquid for 1 h while under a weight exerting a force of 20 g/cm².³⁰ In both tests, the results were given in units of grams of liquid absorbed per gram of polymer. Note that, before modification, the AAP of the polymer was significantly lower than the FSC, indicating that the force of the weight squeezed out much of the absorbed liquid. However, after modification, the AAP was nearly equal to the FSC, indicating that the alkylene carbonate had reacted to create a high density of diester cross-links on the surface of the powder. These cross-links act as a hard shell, reducing the tendency of the liquid-swollen material to deform under an applied weight.

Reactions with Aliphatic Alcohols and the Synthesis of Polycarbonates

Five-membered alkylene carbonates react with aliphatic alcohols differently than with their aromatic analogues. Whereas EC reacts with phenol to yield 2-phenoxyethanol via alkylation and loss of carbon dioxide,^{15–17} EC reacts with methanol via the generalized transesterification route shown in Figure 4a. The

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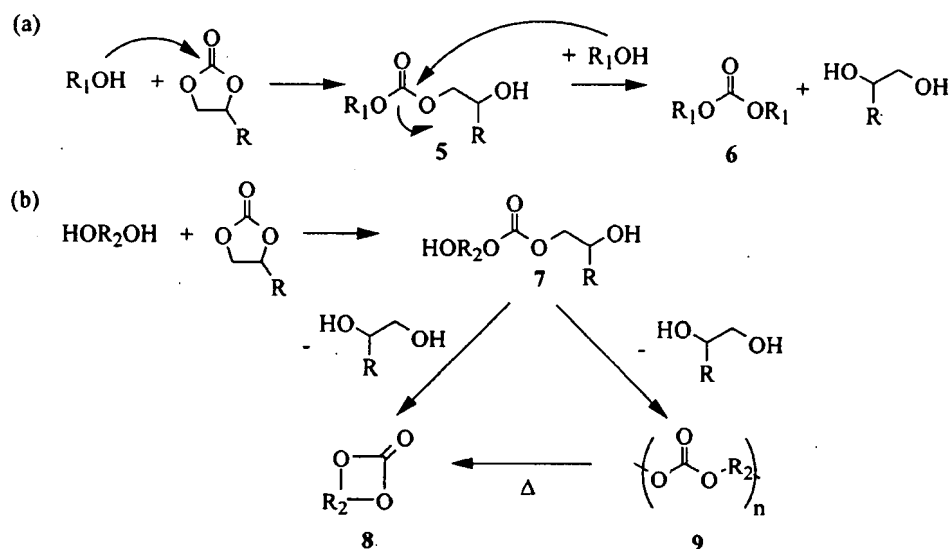


Figure 4. Reactions with aliphatic hydroxyls give dialkyl carbonates, 6, whereas reactions with aliphatic diols give other cyclic carbonates, 8, and/or polycarbonates, 9. Note that there are two possible structural isomers of species 5.

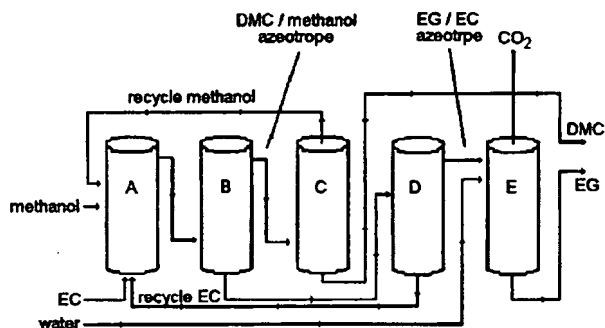


Figure 5. Process diagram for the production of DMC from EC and methanol.

Table 3. Reactions of EC with Various 1,3-Diols^a

$\text{EC} + \text{Diol} \xrightarrow{-EG} \text{Cyclic Carbonate}$							bp (°C)	yield (%)
R ₁	R ₂	R ₃	R ₄	R ₅	R ₆			
CH ₃	CH ₃	H	H	CH ₃	H		197	39.8
CH(CH ₃) ₂	H	CH ₃	CH ₃	H	H		232	59.6
CH ₃	H	H	H	H	H		203	35.1
H	H	C ₂ H ₅	C ₄ H ₉	H	H		262	59.6
C ₃ H ₇	H	C ₂ H ₅	H	H	H		244	76.2

^a Note that reaction yield is relative to the amount of 1,3-diol used.

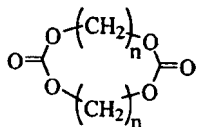
resulting mixture, which contains unreacted EC and methanol in addition to dimethyl carbonate (DMC) and byproduct ethylene glycol (EG), is purified by means of the process diagram shown in Figure 5.³¹ In this process, the reactants are continually fed (5:1 methanol/EC mole ratio) through a catalyst bed consisting of a weakly basic solid support catalyst such as triphenylphosphine on poly(styrene-co-divinylbenzene) at a temperature of 125 °C and a pressure of 100 psig (reactor unit A). The resulting mixture, containing ~20% (by weight) DMC is then distilled at atmospheric pressure to remove DMC and methanol as an azeotropic mixture (reactor unit B). Methanol is then removed by distillation at 150 psig and recycled (reactor C). The purified DMC is a useful reactive intermediate in the synthesis of polycarbonate diols.

Five-membered alkylene carbonates can also be reacted with diols to form other alkylene carbonates or polycarbonates, as shown in Figure 4b. In this regard, alkylene carbonates can be used in lieu of more traditional reactants such as dialkyl carbonates or phosgene.³² In such a process, the yield of alkylene carbonate produced is dependent on the boiling point difference between the reactant and byproduct diols. Researchers at Huntsman have reacted several 1,3-diols with 15% excess EC in the presence of titanium(IV)isopropoxide at 120–150 °C and 15–30 mmHg to prepare six-membered alkylene carbonates (1,3-dioxan-2-ones).³³ The results are shown in Table 3. In each case, the

resulting six-membered alkylene carbonate (~99% purity) was obtained by short-path distillation at temperatures in the range of 150–200 °C at 1–2 mmHg. In certain cases, a mixture of cyclic carbonate and polymer was obtained. However, distillation conditions were sufficient to convert any polymer to the analogous cyclic carbonate such that only catalyst residue remained undistilled. Slight decomposition of polymer or cyclic carbonate to carbon dioxide during distillation was not taken into account. For instances in which the boiling point difference between the 1,3-diol reactant and the byproduct EG (bp = 197 °C) was small, yields of cyclic carbonate were low. This is because considerable amounts of 1,3-diol were removed from the system along with the EG distillate.

Transesterification of 1,2-diols by reaction with carbonates, cyclic or linear, gives five-membered alkylene carbonates almost exclusively. A well-known example is the reaction of dimethyl carbonate (DMC) with propylene glycol to yield PC.³⁴ In contrast, transesterification of 1,X-diols, where X ≥ 4, by reaction with carbonates produces polycarbonates almost exclusively. Only when more reactive sources of carbonate are employed, such as phosgene, are seven- and higher-membered cyclic carbonates obtained in appreciable yield. For instance, Matsuo et al. reacted phosgene trimer with 1,4-butanediol at 45–50 °C and in the presence of chloroform solvent to obtain the seven-membered cyclic carbonate 1,3-dioxepan-2-one in 30%

yield (70% yield of polycarbonate).³⁵ In contrast, when they employed DEC in lieu of phosgene, a mere 2.7% yield of cyclic carbonate was obtained. Interestingly, further analysis of the DEC reaction product revealed that the cyclic carbonate was not the intended seven-membered ring, but the 14-membered dicarbonate ring shown below



in which $n = 4$.³⁵ Similar results were obtained by Kricheldorf and co-workers upon reaction of DEC with 1,10-decanediol. Partial depolymerization of the product at 200–310°C followed by short-path distillation afforded the product cyclobis(decamethylene carbonate) in 9.2% yield.³⁶

Given the above findings, it is not surprising that transesterification of 1,3-diols by reaction with carbonates, cyclic or linear, yields a mixture of cyclic carbonate monomer and polymer. Although a polycondensation mechanism is at work, ring-opening polymerization of the cyclic monomer is also likely given the reaction conditions and catalysts often employed. Therefore, it is necessary to investigate the ring-opening polymerization behavior of the intended cyclic carbonate to explain the above observations. Keul and co-workers³⁷ have found that the thermodynamics of alkylene carbonate polymerization is analogous to that of lactones in that, because of increased ring strain, six- and higher-membered alkylene carbonates tend to polymerize much more readily than five-membered alkylene carbonates. This finding is consistent with that of other researchers, who have found that the analogous polymerization of five-membered alkylene carbonates such as EC and PC is often slow and plagued by side reactions that introduce ether linkages into the material.³⁸ This topic will be covered in more detail in a later section. In contrast, six-membered alkylene carbonates can be homopolymerized quite easily with few, if any, ether linkages by either anionic,³⁹ cationic,^{39,40} or complexation-type⁴¹ means.

In addition to ring size, the degree to which polymer is formed in the transesterification of 1,X-diols by reaction with alkylene carbonates also depends on the number and nature of substituents found on the cyclic carbonate product. This is most evident with regard to the synthesis of six-membered alkylene carbonates. The results of Matsuo and co-workers support this observation.⁴² In their study, six-membered alkylene carbonates were synthesized from ethyl chloroformate with varying substituents at the 5-position. Each was polymerized in THF via potassium *tert*-butoxide initiator at 0 °C. After 1 h, the reaction was terminated by addition of a methanol/phosphoric acid mixture and the percent monomer conversion was determined by ¹H NMR spectroscopy. The percent monomer conversion was found to decrease with increasing size of the substituents at R₃ and R₄. For R₃ = R₄ = CH₃, for example, a 96% conversion was observed. For R₃ = R₄ = C₆H₅, only a 32% conversion of monomer was observed.

On the basis of the above results, particular 1,3-diols can be chosen to give polycarbonates or six-membered alkylene carbonate monomers almost exclusively. If only lightly substituted six-membered alkylene carbonates

such as that for which R₁ = CH₃ and R₂₋₆ = H (5-methyl-1,3-dioxan-2-one) are desired, one must depolymerize the resulting polycarbonate in the manner detailed by Kricheldorf et al.³⁶ with the exception that most polycarbonates synthesized from 1,3-diols unzip to give the cyclic monomer under milder conditions (150–200 °C). Unlike other classes of polymers, many polycarbonates prepared from 1,3-diols can be unzipped quite easily and selectively, giving the cyclic monomer in high yields.^{32a,43} The result is a cyclic carbonate monomer that can be repolymerized via anionic polymerization or other ring-opening technique to give a well-defined material whose molecular weight can be controlled quite well. Because the polymers produced in the manner illustrated in Figure 4b typically have molecular weights in the range of 1000–2500,⁴⁴ the monomer must be recovered and repolymerized by means of a ring-opening technique if higher molecular weights are desired. A considerable amount of information concerning the synthesis of cyclic five- and six-membered alkylene carbonates and the ring-opening polymerization of such species to yield polycarbonates can be found in a recent review by Rokicki.⁴⁵

Because they are hydroxyl-terminated, polycarbonates produced by the transesterification of diols by reaction with alkylene carbonates find employment as spacers in the synthesis of polyurethanes.^{32b,46} Although polycarbonates prepared from unsubstituted diols (R₁₋₆ = H) can be problematic because of poor solubility and compatibility with solvents and curing agents, this problem can be overcome by introducing alkyl- and hydroxyl-containing substituents wherein at least one of R₁₋₆ is alkyl, hydroxyl, or hydroxyalkyl.⁴⁷ The resultant materials boast high tensile strength, flexibility, and chemical resistance. They find utility in the manufacture of paints, coatings, and adhesives.

Reactions with Aliphatic Amines

As with hydroxy-functional materials, five-membered alkylene carbonates react very differently with aliphatic amines than with their aromatic analogues. They undergo attack at the carbonyl carbon atom followed by ring-opening to give a urethane (carbamate) product, **11** (Figure 6b).⁴⁸ Note that only one of two possible isomers of **11** is shown. Unlike linear carbonates (Figure 6a),⁴⁹ the reaction of alkylene carbonates with amines yields a hydroxy-functional species useful as a reactive intermediate. Although similar products can be obtained via the reaction of diols with urea,⁵⁰ such reactions generally require higher temperatures (120–170 °C) and evolve ammonia as a byproduct. In addition, if hydroxyalkylurethanes are desired, care must be taken to prevent ring closure, which yields an alkylene carbonate and a second mole of ammonia byproduct.

Unlike reactions that occur in the presence of aliphatic alcohols, the hydroxyalkylurethane species produced does not usually undergo further reaction with a second mole of amine to produce a urea or imidazolidinone, except at temperatures ≥ 150 °C (Figure 6c).⁵¹ For R₂ = H, cyclization of **11** yields an oxazolidinone, **12**, with loss of water. Reaction with a second mole of amine gives a hydroxyalkylurea (not shown), which also undergoes cyclization with loss of water to yield the imidazolidinone or cyclic urea, **13**. Note that this reaction occurs in the absence of catalyst. Should a low-boiling amine such as methylamine be employed, high pressure is required to keep the reaction mixture condensed at the necessary temperatures.

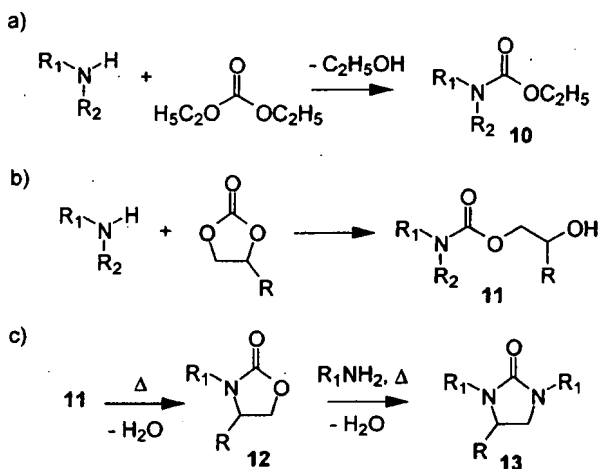
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Figure 6. (a) Reaction of linear carbonates (DEC shown) with amines gives urethanes, **10**. (b) Reaction of alkylene carbonates with aliphatic amines gives hydroxyalkylurethanes, **11**. (c) Heating **11**, where $R_2 = H$, in the absence of excess amine results in cyclization and loss of water to give oxazolidinones, **12**, whereas heating in the presence of excess amine ultimately yields imidazolidinones, **13**.

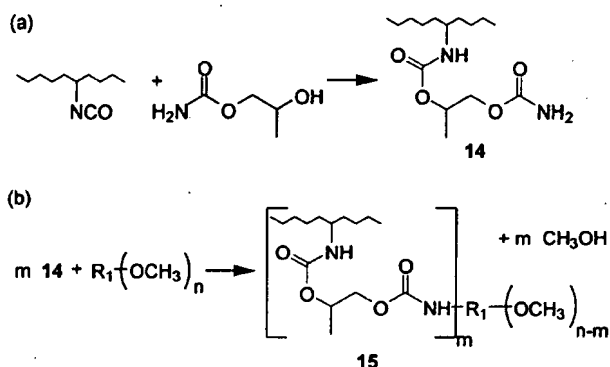
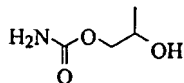


Figure 7. Synthesis of polyurethane resin for automotive coatings. (a) Reaction of HPC with isocyanate-functional polymers. (b) Reaction of carbamate-functional polymer, **14**, with cross-linking agent to give cross-linked polymer **15**.

Five-membered alkylene carbonates will react with primary and some secondary amines at room temperature. Although most reactions can be accomplished without the aid of a catalyst, alkali materials can be employed to increase the reaction rate.⁵² The reaction is accompanied by an exotherm that must be controlled by monitoring the addition rate of one component into the other.⁵³ An example is the reaction of PC with ammonia to generate hydroxypropylcarbamate (HPC)^{48a}



as a 50/50 \pm 10% mixture of isomers (only one of which is shown). This material has found use in the automotive coatings industry in methods for preparing novel polyurethane resins.⁵⁴ For instance, researchers at BASF have investigated reactions of HPC with isocyanate-functional polyacrylates to prepare carbamate-functional polymers as illustrated in Figure 7a.^{54d} The resulting products of general structure **14** were then mixed with a cross-linking agent bearing methoxy substituents such as hexamethoxymethyl melamine (*n*

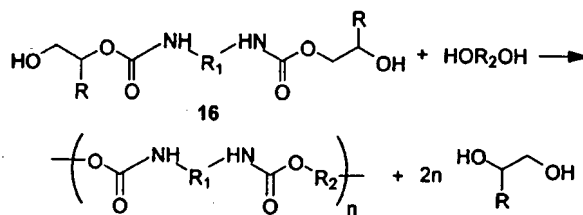
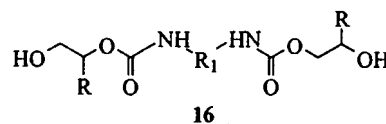


Figure 8. Reaction of a bis(hydroxyalkyl)urethane, **16**, with a polyol to produce a polyurethane.

= 6) during spray application to a surface. Subsequent baking or curing of the mixture gave urethane-cross-linked coatings, **15** (Figure 7b), in which $m = 3-4$. Although similar coatings can be obtained simply by mixing a polyisocyanate with a polyol in a spray applicator, the polyisocyanate fumes generated under such conditions can be dangerous and difficult to contain. In the above example, however, the isocyanate has been converted to the much less hazardous material **14** under controlled laboratory conditions prior to application, eliminating the dangers previously associated with this industry. The resulting coating exhibits excellent resistance to environmental etch (acid rain), scratch and mar, salt corrosion, and hydrolysis,⁵⁵ all necessary of coatings in the automotive industry.

It is well-known that polymers containing urethane linkages in their backbones can be prepared by the reaction of a diisocyanate with a polyol. However, it was discovered that the toxic diisocyanate used in this process could be replaced with the analogous diamine with the assistance of alkylene carbonates. Researchers at King Industries reacted alkylene carbonates with aliphatic diamines to give difunctional hydroxyalkyl urethanes of structure **16**.



which act as blocked isocyanates.⁵⁶ **16** was then reacted with a polyester polyol in the presence of a tin transesterification catalyst at 160 °C to produce the desired polyurethane with removal of the byproduct glycol by distillation (Figure 8). Thus, a polyurethane was prepared without the need for isocyanates.

In addition to polyurethanes, the above technology has also been applied to the modification of amino acids for the production of biocompatible polymers⁵⁷ and dispersants for use in lubricating oils, hydraulic oils, and gasoline. For instance, researchers at Chevron have capped polyisobutylene with maleic anhydride followed by reaction with ethylene amines such as triethylene tetraamine (TETA) to form polyalkylene succinimides. They have found that reaction of EC with the resulting secondary and primary amines yields hydroxyalkylurethane adducts with superior dispersant characteristics (Figure 9).⁵⁸ These adducts are useful in reducing engine deposits such as sludge and ash resulting from incomplete combustion. Modification via ethylene carbonate also improves the compatibility of the polyalkylene succinimide dispersant with other components of the formulation.

Alkylene carbonates can also be reacted with amines that contain hydroxyl groups to give added functionality to the urethane product. However, reactions with β -hy-

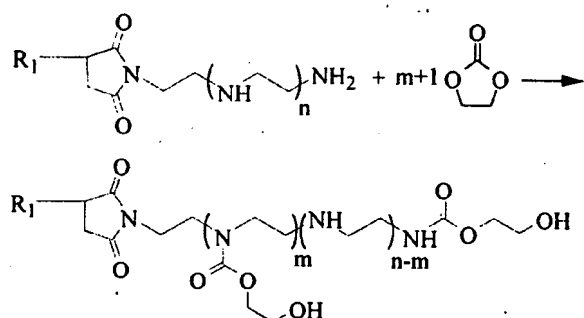


Figure 9. Modification of polyalkylenesuccinimide dispersants by reaction with EC, $n = 3-5$, $m = 1, 2$. R_1 = polyisobutylene backbone.

doxyalkylamines such as ethanolamine are often accompanied by cyclization and loss of glycol to give oxazolidinones under mild heating (Figure 10).⁵⁹ Oxazolidin-2-one ($R_1 = H$) in particular can also be prepared by the reaction of EC with urea.⁶⁰ Such materials and their derivatives find use as medicinal actives for the treatment of bacterial infections, arthritis, and toxicity caused by chemotherapy.⁶¹

Although the bulk of this section, and indeed most of this review, has focused on the reactive applications of five-membered alkylene carbonates, EC and PC in particular, it should be noted that six-membered cyclic carbonates (1,3-dioxan-2-ones) can also be reacted with aliphatic amines.⁶² Tomita et al. have reacted allyl-functional five- and six-membered alkylene carbonates with *n*-hexylamine and benzylamine in the absence of catalyst at various temperatures to compare their reactivities.^{62a} By monitoring the carbonate conversion by ¹H NMR spectroscopy and assuming second-order kinetics, they determined that the rate constant ratio, $K = k_1/k_2$, where k_1 and k_2 are the rate constants for the reaction of six- and five-membered alkylene carbonates, respectively, is 28–60 depending on the reaction temperature and amine employed. Thus, the 1,3-dioxan-2-ones react much more quickly with amines than do the corresponding 1,3-dioxolan-2-ones, reaching completion in shorter times and at lower temperatures. Should such materials become available commercially, they might even be viable in spray coating applications for large surfaces, such as airport terminal flooring, which must cure quickly and at ambient temperatures.

Ring-Opening Polymerization of Alkylene Carbonates

As stated earlier, five-membered alkylene carbonates undergo ring-opening polymerization with difficulty. Soga and co-workers were among the first researchers to report this behavior.³⁸ In fact, the ceiling temperature, t_c , for the process is quite low. For instance, a t_c of only 25 °C was reported for the ring-opening polymerization of EC.⁶³ Nevertheless, EC and other 1,3-dioxolan-2-ones have been polymerized at temperatures exceeding 100 °C. To understand this apparent inconsistency, it must be noted that polymerization involves loss of carbon dioxide such that the polymer produced contains both carbonate and ether linkages.

It has recently been proposed that the anionic ring-opening polymerization of EC takes place according to the mechanism illustrated in Figure 11.^{63,66} Following initiation (Figure 11a), the propagating chain can add EC via attack at the carbonyl (Figure 11b) or alkylene

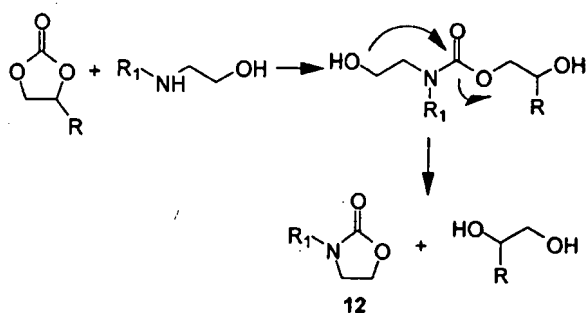


Figure 10. β -Hydroxyalkylamines often undergo cyclization to oxazolidinones, 12, prior to reaction with alkylene carbonates.

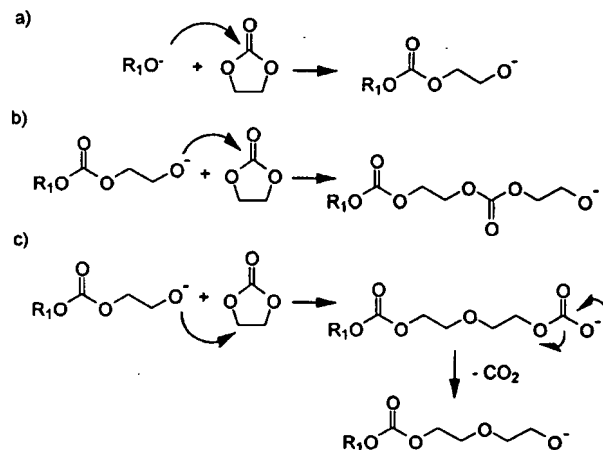


Figure 11. (a) EC ring-opening initiated by an anionic species. (b) Propagation via carbonyl attack, yielding a carbonate linkage. (c) Propagation via alkylene attack, yielding an ether linkage and loss of carbon dioxide.

(Figure 11c) carbon, resulting in the production of a carbonate or ether linkage, respectively. Assuming that ΔS of decarboxylation is positive,⁶³ polymerization of 1,3-dioxolan-2-ones at temperatures above t_c for traditional ring-opening does not violate thermodynamic principles. However, data generated by Vogdanis et al.⁶⁴ reveal that the polymerization process is somewhat different from that illustrated in Figure 11. Recognizing that the entropy of ring-opening polymerization, ΔS_p , is positive and using the well-known relation

$$\Delta G_p = \Delta H_p - T\Delta S_p$$

it can be said that, for the process to occur spontaneously ($\Delta G_p < 0$), the enthalpy of ring-opening polymerization, ΔH_p , must be negative. This was not found to be the case, as ΔH_p values of 124.6, 125.6, and 112.5 kJ/mol were measured for the ring-opening polymerization of EC, resulting in pure poly(ethylene carbonate), at temperatures of -73, 25, and 170 °C, respectively. Thus, the reaction scheme illustrated in Figure 11b is not possible according to thermodynamic principles.

Alternatively, Vogdanis and co-workers⁶⁵ proposed that the carboxylate ion produced via the scheme illustrated in Figure 11c can add an additional molecule of EC as well as undergo decarboxylation. Note that this is very different from the mechanism given in Figure 11, for which Lee and co-workers⁶³ claim that the alkylate ion generated as a result of decarboxylation, rather than the carboxylate ion, is the active chain-propagating species. For the thermodynamic reasons discussed above, Vogdanis and co-workers state that

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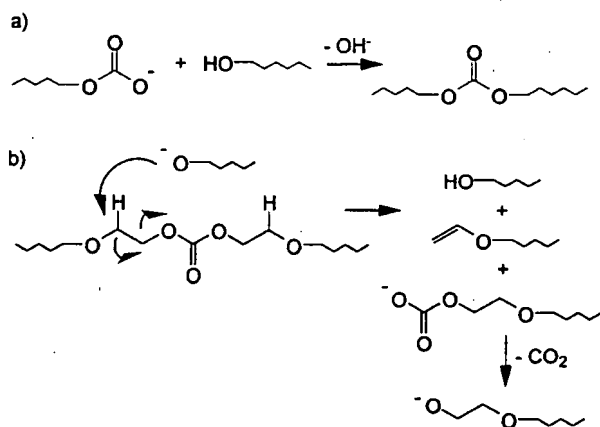
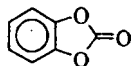


Figure 12. (a) Reaction of carboxylate ion with the hydroxy terminus of another polymer chain. (b) Mechanism proposed by Lee et al.⁶³ for stage two polymer degradation.

only one carbonate linkage can be formed in the aforementioned manner before decarboxylation and subsequent ether linkage formation. Thus, the fraction of carbonate linkages in the polymer relative to ether linkages cannot exceed 50%. It should also be noted that evidence suggests that the carboxylate ion shown in Figure 11c can react with the hydroxy terminus of another polymer chain, connecting two chains through a carbonate linkage (Figure 12a).⁶⁶ At this time, it should be reiterated that, if polymerization is initiated by an aromatic species such as the phenolate ion,⁶⁷ then initiation involves CO_2 loss exclusively, in keeping with the method of alkylene carbonate alkylation discussed earlier (Figure 2).

Interestingly, Lee and co-workers have studied the polymerization of EC initiated by KOH at various temperatures (150–200 °C) and ratios of carbonate to initiator (1000:1 to 20:1) and discovered that the reaction can be described as a two-stage process. In this manner, the final polymer obtained is the result of not only initiation and propagation but also chain cleavage.⁶³ In the first stage, the molecular weight of the polymer increases with reaction time to a maximum molecular weight in the range of 1000–9000 depending on the carbonate-to-initiator ratio employed. The material generally has a carbonate-to-ether linkage ratio of about 2 (30–32% carbonate), which remains fairly constant until approximately 90–100% monomer conversion. In the second stage, the molecular weight and carbonate content of the material decrease significantly with continued heating. In addition, the presence of a vinyl moiety can be seen by NMR analysis. To account for these observations, they proposed the chain cleavage mechanism shown in Figure 12b.

As seen with six-membered cyclic carbonates, polymerization of 1,3-dioxolan-2-ones is dependent on the number and size of substituents on the carbonate ring. Whereas EC and PC can be polymerized to molecular weights of > 50 000, the highly substituted benzo-1,3-dioxolan-2-one



does not polymerize at all.⁶⁸

It is widely recognized that the preferred method of producing poly(alkylene oxide-co-alkylene carbonate)s

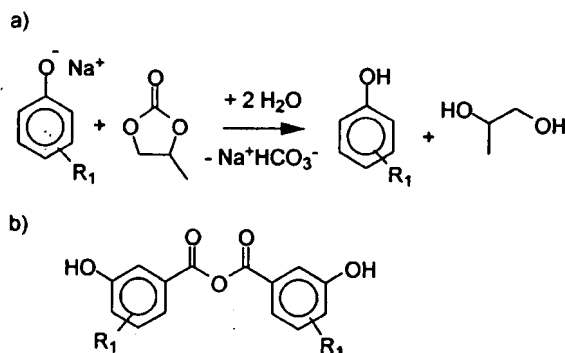


Figure 13. (a) Proposed mechanism of PF cure acceleration via PC hydrolysis. (b) Cross-linking structure detected by Pizzi et al.^{77a} R_1 represents the remainder of the PF resin.

is via the copolymerization of the desired alkylene oxide, for instance, ethylene oxide (EO), and CO_2 . Both academic and industrial researchers have studied this type of reaction in detail. Typically, the reaction is performed within the temperature range 75–150 °C under pressures of 100–500 psi. Useful initiators for the process include zinc(II)phenoxides,⁶⁹ zinc dicarboxylates,⁷⁰ β -diiminate zinc complexes,⁷¹ stannate salts,⁷² diethylzinc,⁷³ and triethylaluminum,⁷³ to name but a few. A more complete listing is presented in a review by Darensbourg et al.⁷⁴ The resulting materials have found utility as nonionic surfactants,⁷² binders for glass and ceramics,⁷⁵ and as possible cosolvents for use in supercritical CO_2 applications.⁷⁶ However, the molecular weight of such materials is often difficult to control. Although it is debatable whether polymerization of the five-membered cyclic carbonates offers better molecular weight control, such processes do offer a low-pressure alternative to those not able or willing to employ the pressures required of alkylene oxide/ CO_2 copolymerization.

Unlike the 1,3-dioxolan-2-ones, six- and seven-membered alkylene carbonates polymerize much more rapidly and selectively. The details of such polymerizations are described in a previous section.

Alkylene Carbonates as Cure Accelerators

In addition to their utility as chemical intermediates, alkylene carbonates also find use as cure accelerators of phenol-formaldehyde (PF)⁷⁷ and sodium silicate (SS)⁷⁸ resin systems, which are widely used in foundry sand and wood binder applications. Although the effect of alkylene carbonates, particularly PC, on the reaction of phenol and formaldehyde in the presence of sodium hydroxide has been studied for some time, the exact mechanism responsible for cure acceleration is still a subject of debate. Unfortunately, analysis of cured PF resins has been hampered by the fact that such materials contain numerous isomers and are only sparingly soluble. Tohmura and co-workers^{77c} claim that propylene carbonate is quickly hydrolyzed to propylene glycol and sodium hydrogen carbonate (Figure 13b) when exposed to the conditions required for PF cure. Thus, it is the sodium hydrogen carbonate byproduct, a cure accelerator in its own right, that is responsible for the accelerated cure. Although Pizzi et al. agrees that PC hydrolysis does occur to some extent, they propose mechanisms in which the cyclic carbonate actively participates in bridging reactions.^{77a} On the basis of ^{13}C NMR observations, they claim the existence of anhydride bridges (Figure 13b) not found when sodium

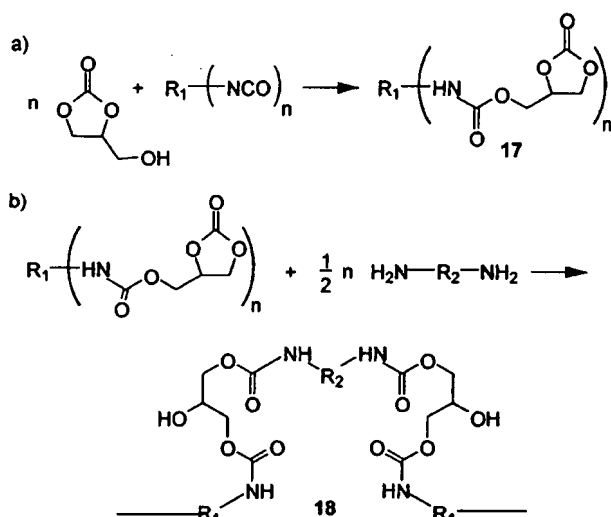
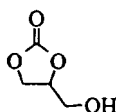


Figure 14. Reaction of GC with an n -functional isocyanate creates an n -functional alkylene carbonate, 17. Reaction of 17 with a diamine gives a useful polyurethane resin, 18. Note that 18 can be linear ($n = 2$) or a network ($n > 2$).

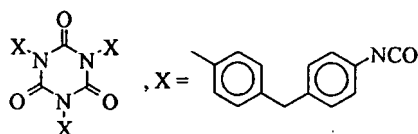
hydrogen carbonate alone is employed as an accelerant.^{77d} A few observations made by Park and co-workers^{77e} seem to support this idea; however, they concede that more conclusive evidence is needed. It might be possible that both mechanisms are at work.

Five-Membered Alkylene Carbonates that Include Added Functionality

No review of this nature would be complete without a brief discussion of alkylene carbonate derivatives aside from the simple alkyl-substituted cyclics. With this in mind, many derivatives of 1 have been developed in recent years that contain added functionality, that is, 1,3-dioxolan-2-one derivatives that contain reactive groups in addition to the carbonate ring itself. Examples include vinyl moieties, esters, ethers, and alcohols. Of these, only glycerol (glycerin) carbonate (GC)



is available commercially. The material can be synthesized by the reaction of glycerin with a carbonate source such as phosgene, a dialkyl carbonate,⁷⁹ or an alkylene carbonate;⁸⁰ by reaction of glycerin with urea,⁸¹ carbon dioxide,⁸² and oxygen;⁸² or by reaction of carbon dioxide with glycidol. Because it contains a hydroxy-functional substituent, GC can be reacted with anhydrides,⁸³ acyl chlorides,^{79a} isocyanates,⁸⁴ and the like. For instance, researchers at Imperial Chemical Industries reacted GC with the multifunctional isocyanate polymeric MDI



in the presence of potassium acetate to create a multifunctional alkylene carbonate of the general structure 17, shown in Figure 14a.^{84a} The reaction of GC with

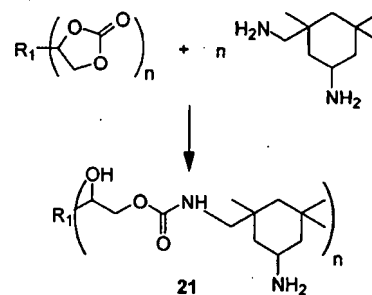
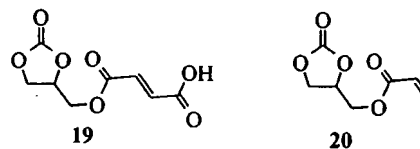


Figure 15. Reaction of multifunctional alkylene carbonates with IPDA to produce an amine-functional cross-linking agent, 21. Note that only one structural isomer of 21 is shown.

isocyanates occurs at room temperature or with slight heating and is generally accompanied by an exotherm such that the controlled addition of one component into the other is desired. By monitoring for the presence of isocyanate by IR spectroscopy, the necessary reaction time can easily be determined.

The multifunctional carbonates prepared by means of the above process are useful as blow promoters in the preparation of polymeric foams,^{84a} or they can be reacted with aliphatic diamines to prepare polyurethane resins, 18 (Figure 14b).⁸⁵ Although specific details concerning the reaction of alkylene carbonates with amines were discussed in a previous section, it should again be noted that a promoter is not required and that a temperature increase, sometimes as much as $\Delta t = 75^\circ\text{C}$, is observed upon mixing. The components can be mixed in the presence of a polar solvent such as DMF with stirring until a high viscosity is obtained. Once cured at $50\text{--}75^\circ\text{C}$ for 12–48 h, the resulting resins can be readily cast into films with excellent clarity and tear resistance or extruded into fibers having high tensile strengths.^{85a}

Vinyl-functional alkylene carbonates, useful in the preparation of polymers that contain alkylene carbonate pendant groups, can also be prepared from GC. Two examples are the reaction of GC with maleic anhydride and acrylyl chloride to produce the acrylate-functional cyclic carbonates 19 and 20, respectively.^{83a}



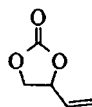
Although the transesterification of alkyl esters such as dimethyl maleate or methyl acrylate by reaction with GC represents an obvious means of obtaining the above materials, the temperatures required of such processes ($>100^\circ\text{C}$) result in unwanted polymerization of both the reactant and product species, even in the presence of well-known radical inhibitors such as 2,6-di-*tert*-butyl-*p*-cresol.^{83a} In addition, the synthesis of vinyl-functional alkylene carbonates such as 19 and 20 is greatly complicated by the fact that such materials cannot be purified by distillation and must be stored at temperatures $< 0^\circ\text{C}$.^{86,87} In fact, these and similar species are known to undergo polymerization much more readily than the analogous underivatized vinyl monomers.⁸⁸

Despite the synthetic challenges, the novel polymers produced from the above monomers can be modified for use in a wide range of applications by reacting the alkylene carbonate pendant moieties employing any of the synthetic techniques described above. For instance,

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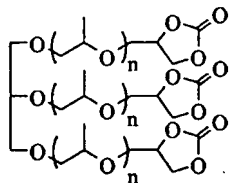
several researchers have documented the reaction of alkylene carbonate-containing polymers with amines and diamines to produce graft and network polymers.^{87,88b,89}

Vinyl-functional alkylene carbonates can also be prepared from the corresponding epoxides in a manner similar to the commercial manufacture of EC and PC via CO₂ insertion.¹ The most notable example of this technology is the synthesis of 4-vinyl-1,3-dioxolan-2-one or vinyl ethylene carbonate (VEC) from 3,4-epoxy-1-butene.



Originally reported by Bissinger and co-workers in 1947⁹⁰ and later by DuPont,⁹¹ much of the latest research involving this molecule has been performed by Webster and Crain at Eastman. Preliminary studies have found that VEC can be copolymerized with readily available vinyl monomers useful in the coatings industry, such as styrene, alkyl acrylates and methacrylates, and vinyl esters.⁹² With the exception of styrene, the authors found that VEC will undergo free-radical solution or emulsion copolymerization, although not quantitatively, with all comonomers studied to produce polymeric species with a pendant five-membered alkylene carbonate functionality that can be further cross-linked by reaction with amines.⁹³ A more complete review of vinyl-functional five-membered alkylene carbonates and their potential in the manufacture of novel cross-linkable polymers has been provided by Webster and Crain.⁹⁴

Although not yet commercially available, multi-alkylene carbonates can also be prepared from epoxy resins via CO₂ insertion.^{54c,95} An example is the insertion of 3 mol of CO₂ into Heloxy Modifier 84 (Shell), a trifunctional epoxy-terminated polyoxypropylene based on glycerine. The result is the trifunctional alkylene carbonate shown below



where $n \approx 8$. As with other cyclic carbonates, these and similar materials can be further reacted with amines to yield novel polyurethanes.^{95b-d} The extensive body of research performed by Endo and co-workers in this area has led to a much greater understanding of the chemistry involved, thereby allowing its emergence in industry. For example, researchers at Fiber-Cote have reacted this material with isophorone diamine (IPDA) to prepare the amine-functional adduct shown in Figure 15a.^{54c} The reaction takes advantage of the significant difference in the reactivity of the aliphatic amine versus the cycloaliphatic amine with alkylene carbonates such that only the aliphatic amine participates in reaction. The result is an adduct that can be reacted with epoxy resins to form useful urethane coatings without the need for isocyanates.

Future Outlook

The reactive applications of alkylene carbonates is exhaustive. As new applications continue to be developed regarding commercially available alkylene carbonates, the demand for carbonate-functional cross-linkable polymers, polycarbonates, and other functional derivatives such as those discussed in previous sections is on the rise. Large-scale production of these novel substances such that they can be made available at reasonable costs is the challenge that faces future researchers in this field.

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Anionic Ring-Opening Polymerization of Cyclic Thiocarbonates Containing Norbornene and Norbornane Groups Undergoing Volume Expansion on Polymerization

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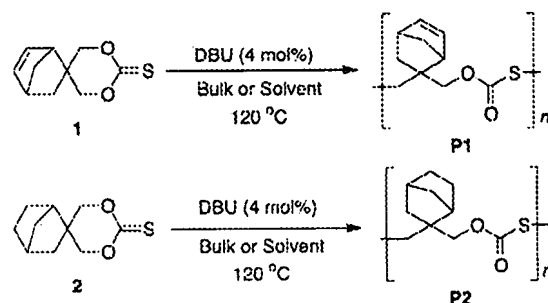
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Six-membered cyclic thiocarbonate derivatives, 5,5-(bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxane-2-thione (**1**) and 5,5-(bicyclo[2.2.1]heptan-5,5-ylidene)-1,3-dioxane-2-thione (**2**) underwent anionic ring-opening polymerization initiated by 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) to afford polythiocarbonates accompanying 12.3 and 12.6% volume expansion, respectively.

Common vinyl monomers such as styrene and methyl methacrylate undergo polymerization with volume shrinkage.¹ Thermosetting resins such as epoxides also show 4–5% volume shrinkage during the curing process. The occurrence of the volume shrinkage of the monomers and resins induces serious problems in their industrial applications for composites, adhesives, coatings, precision castings, and sealant materials. Cyclic carbonates undergo cationic and anionic ring-opening polymerizations accompanying volume expansion, which can be accounted for by difference in strength of intermolecular dipole-dipole interactions between monomers and polymers. For example, a six-membered cyclic carbonate bearing norbornene moiety undergoes 8.2% volume expansion during anionic polymerization.² Recently, sulfur-containing polymers are gaining importance due to their excellent optical and thermal properties.³ In the course of our work on ring-opening polymerization of cyclic carbonates, we have designed a sulfur analogue of cyclic carbonate, i.e., cyclic thiocarbonate, which exhibits a unique reactivity. Anionic ring-opening polymerization³ of 1,3-oxathian-2-one proceeds via selective ring-opening with C–S bond cleavage to afford the corresponding polythiocarbonate. Cationic ring-opening polymerization⁴ of 5,5-dimethyl-1,3-dioxane-2-thione proceeds accompanying isomerization of thiocarbonate group via a living process to afford polythiocarbonate.⁵ We also studied cationic ring-opening polymerization of novel six-membered cyclic thiocarbonate derivatives, 5,5-(bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxane-2-thione (**1**) and 5,5-(bicyclo[2.2.1]heptan-5,5-ylidene)-1,3-dioxane-2-thione (**2**).⁶ Unidentified products were obtained from the reaction of **1** initiated by trifluoromethanesulfonic acid (TfOH), methyl trifluoromethanesulfonate (TfOMe), boron trifluoride etherate (BF₃OEt₂), or triethyloxonium tetrafluoroborate (Et₃OB⁺F₄); however, **1** underwent the cationic ring-opening polymerization by using methyl iodide as initiator to afford polythiocarbonate. In this study, for developing a new polymerization system with volume-expansion, we attempt anionic ring-opening polymerization of **1** and **2** as shown in Scheme 1. We report the thermal properties of the obtained polythiocarbonates and the volume change during polymerization to reveal the effect



Scheme 1.

of introduction of a thiocarbonate group instead of a carbonate one.

Anionic ring-opening polymerization⁷ of **1**⁶ and **2**⁶ was carried out with 4 mol% of 1,8-diazabicyclo[5.4.0]-7-undecene (DBU)² at 120 °C as summarized in Table 1. The polymerization of **1** and **2** proceeded in all cases except run 4, wherein the high melting point (215 °C)⁶ may inhibited the polymerization of run 4 in Table 1. The molecular-weight-distributions (M_w/M_n) of the obtained polymers were somewhat broad (1.40–1.48). The low polymer yields may be due to the chain-transfer reactions such as back-biting reaction. The polymer could be isolated by precipitation with methanol, and exhibited good solubility in common organic solvents such as THF, chloroform, and dichloromethane. The structures of the obtained polymers were confirmed by NMR and IR spectroscopy. **P1** and **P2** exhibited ¹³C NMR signals at 154 ppm, which is assignable to carbonyl carbon. In addition, an absorption band based on carbonyl group was observed at 1743 cm^{−1} in their IR spectra. These data may suggest that the polymerization proceeded accompanying the isomerization of thiocarbonate group as observed in the anionic

Table 1. Anionic ring-opening polymerization of **1** and **2**^a

Run	Monomer	Time/h	Solvent	Yield ^b /%	M_n^c	M_w/M_n^c
1	1	1	none	25	15200	1.48
2	1	12	toluene	38	8800	1.44
3	1	12	DMF	38	8600	1.47
4	2	1	none	no reaction		
5	2	12	toluene	8	7100	1.43
6	2	12	DMF	22	11800	1.40

^aTemp. 120 °C, monomer 1.00 mmol, solvent 0.20 mL, initiator DBU 0.040 mmol. ^bCalculated from the amounts of the monomer and polymer isolated by preparative high performance liquid chromatography eluted with chloroform.

^cEstimated by size exclusion chromatography (SEC) eluted with THF at 40 °C based on polystyrene standards.

polymerization of 1,3-dioxane-2-thione.⁸

Thermal behavior of the polymers was evaluated by TGA and DSC under nitrogen as summarized in Table 2. P1 and P2 lost their 10% weight at 258 and 261 °C, respectively. The high thermal stability of P1 and P2 compared to the corresponding polycarbonate P3² may be attributable to the introduction of sulfur into the polymer backbone.

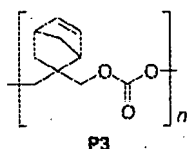
Table 2. Properties of P1–P3

Polymer	Volume change ^a /%	T_g^b /°C	T_{d10}^c /°C
P1	+12.3	82	258
P2	+12.6	82	261
P3 ^d	+8.2	108	207

^aCalculated by the densities of the monomer and polymer.

^bDetermined by differential scanning calorimetry (DSC).

^cDetermined by thermogravimetry (TG). ^dData from reference 2.



Densities of the monomers and the obtained polymers were evaluated by density gradient tubes at 25 °C. The densities of P1 and 1 were 1.14 and 1.30, and those of P2 and 2 were 1.11 and 1.27, respectively. These results indicated that the polymerization of 1 and 2 proceeded with volume expansion as large as 12.3 and 12.6%, respectively, due to the difference in strength of intermolecular dipole-dipole interactions between monomers and the obtained polymers.¹

In summary, six-membered cyclic thiocarbonate derivatives, 5,5-(bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxane-2-thione (1) and 5,5-(bicyclo[2.2.1]heptan-5,5-ylidene)-1,3-dioxane-2-thione (2) underwent anionic ring-opening polymerization to afford the polycarbonates accompanying the isomerization of thiocarbonate group and remaining norbornene and norbornane structures, respectively. The obtained polymer showed good

solubility and high thermal stability. The monomer showed volume expansion during polymerization to lead a new polymerization system with volume expansion.

This article is dedicated to Professor Teruaki Mukaiyama for his 75 th birthday.

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